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(REV. 5-93)U. S. DEPARTMENT OF COMMERCE  
PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

2954/0H643

**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)**INTERNATIONAL APPLICATION NO.  
PCT/EP99/02102INTERNATIONAL FILING DATE  
29 MARCH 1999PRIORITY DATE CLAIMED  
30 MARCH 1998

## TITLE OF INVENTION

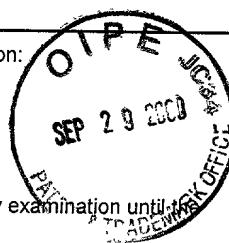
**METHOD OF MAKING POLYMER ELECTROLYTE ELECTROCHEMICAL CELLS**jc930 U.S. PTO  


09/29/00

## APPLICANT(S) FOR DO/EO/US

TOPSOE, Martin; WENDSJO, Asa; YDE-ANDERSEN, Steen

Applicant herewith submits to the United States Designated/Elected office (DO/EO/US) the following items and other information:



1.  This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2.  This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3.  This is an express request to begin national examination procedures (35 U.S.C. 371 (f)) at any time rather than delay examination until expiration of the applicable time limit set in 35 U.S.C. 371 (b) and PCT Articles 22 and 39 (1).
4.  A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5.  A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a.  is transmitted herewith (required only if not transmitted by the International Bureau).
  - b.  has been transmitted by the International Bureau
  - c.  is not required, as the application was filed in the United States Receiving Office (RO/US)
6.  A translation of the International Application into English (35 U.S.C. 371 (c)(2)).
7.  Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a.  are transmitted herewith (required only if not transmitted by the International Bureau).
  - b.  have been transmitted by the International Bureau.
  - c.  have not been made; however, the time limit for making such amendments has NOT expired.
  - d.  have not been made and will not be made.
8.  A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c) (3)).
9.  An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) (**Unsigned**).
10.  A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

## Items 11. to 16. below concern other document(s) or information included:

11.  An Information Disclosure Statement under 37 CFR 1.97 and 1.98 (with references).
12.  An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13.  A FIRST preliminary amendment.
  A SECOND or SUBSEQUENT preliminary amendment.
14.  A substitute specification.
15.  A change of power of attorney and/or address letter.
16.  Other items or information:

EXPRESS MAIL CERTIFICATE  
9/29/00 E2628222953USDate \_\_\_\_\_ Label No. \_\_\_\_\_  
I hereby certify that, on the date indicated above I  
deposited this paper or fee with the U.S. Postal Service  
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of Patents & Trademarks, Washington D.C. 20591-1200  
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Name (Print) \_\_\_\_\_ Signature \_\_\_\_\_

U.S. APPLICATION NO. (if known sec 37 C.F.R. 1.50) <b>097647662</b>	INTERNATIONAL APPLICATION NO.: PCT/EP99/02102	Attorney's Docket Number 2954/0H643-US		
17. [X] The following fees are submitted:		ALCULATIONS      PTO USE ONLY		
Basic National Fee (37 CFR 1.492 (a)(1)-(5)): Search Report has been prepared by the EPO [X] or JPO []		\$840.00		
International preliminary examination fee paid to USPTO (37 CFR 1.482) .....		\$670.00		
No international preliminary examination fee paid to USPTO(37 CFR 4.482) but international search fee paid to USPTO (37 CFR 1.445 (a) (2)...)		\$690.00		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO.....		\$970.00		
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4),.....		\$96.00		
ENTER APPROPRIATE BASIC FEE AMOUNT =		<b>\$840.00</b>		
Surcharge of \$130.00 for furnishing the oath or declaration later than []20 []30 months from the earliest claimed priority date (37 CFR 1.492(e)).		\$		
Claims	Number Filed	Number Extra	Rate	
Total Claims	17-20	0	0 X \$18.00	\$0
Independent Claims	1-3	0	0 X \$78.00	\$0
Multiple dependent claims(s) (if applicable)	+260			\$0
		TOTAL OF ABOVE CALCULATIONS =	<b>\$840.00</b>	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).			\$840.00	
		SUBTOTAL =	<b>\$840.00</b>	
Processing fee of \$130.00 for furnishing the English translation later the [] 20 [] 39 months from the earliest claimed priority date (37 CFR 1.492(f)).		+	\$	
		TOTAL NATIONAL FEE =	<b>\$840.00</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). the assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property		+	\$	
		TOTAL FEES ENCLOSED =	<b>\$</b>	
		Amount to be refunded	\$	
		charged	\$	
<p>a. [X] A check in the amount of <u>\$840.00</u> to cover the above fees is enclosed.</p> <p>b. [] Please charge my Deposit Account No.04-0100 in the amount of \$ to cover the above fees.</p> <p>c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 04-0100. A duplicate copy of this sheet is enclosed.</p>				
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.				
SEND ALL CORRESPONDENCE TO: <b>S. Peter Ludwig</b> Darby & Darby P.C. 805 Third Avenue New York, New York 10022-7513				
SIGNATURE  NAME <b>S. Peter Ludwig</b>				
REGISTRATION NO. 25,351				

09/647662

532 Rec'd PCT/PTC 29 SEP 2000

File No: 2954/0H643

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

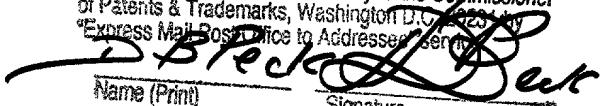
**Martin TOPSOE, Asa WENDSJO, Steen YDE-ANDERSEN**

U.S. Serial No.: To Be Assigned (U.S. National Phase  
of International Application No. PCT/EP99/02102,  
Filed 29 March 1999)

Group Art Unit: To Be Assigned

Filed On: Herewith      Examiner: To Be Assigned

For: **METHOD OF MAKING POLYMER ELECTROLYTE  
ELECTROCHEMICAL CELLS**

EXPRESS MAIL CERTIFICATE  
*9/29/00* Date *SC62822953VS* Label No.  
I hereby certify that, on the date indicated above I  
deposited this paper or fee with the U.S. Postal Service  
& that it was addressed for delivery to the Commissioner  
of Patents & Trademarks, Washington D.C. 20231 by  
Express Mail Post Office to Addressee's service.  
  
Name (Print) *D.P. Beck* Signature *D.P. Beck*

PRELIMINARY AMENDMENT

Hon. Commissioner of  
Patents and Trademarks  
Washington, DC 20231

**BOX PCT  
ATTN: DO/EO/US**

Sir:

Prior to examination, applicants wish to amend the above-identified international application as follows:

IN THE SPECIFICATION:

Page 1, above line 4, insert the heading --Field of the Invention--.

Page 1, above line 7, insert the heading --Background of the Invention--.

Page 5, above line 4, insert the heading --Detailed Description of the Invention--.

U.S. SERIAL NO. To Be Assigned (U.S. National Phase  
of International Application No. PCT/EP99/02102)  
FILED ON: Herewith  
EXAMINER: To Be Assigned  
GROUP ART UNIT: To Be Assigned

**IN THE CLAIMS:**

2. Claim 3, line 1, delete "claim 2" and substitute therefor --Claim 1--.

Claim 5, line 1, delete "any of claims 1 to 4" and substitute therefor --Claim 1--.

Claim 6, line 1, delete "any one of claims 1 to 5" and substitute therefor --Claim 1--.

Claim 7, line 1, delete "any of the preceding claims" and substitute therefor --Claim 1--.

Claim 8, line 1, delete "any one of the preceding claims" and substitute therefor --

Claim 1--.

Claim 10, line 1, delete "claim 8 or 9" and substitute therefor --Claim 8--.

Claim 11, line 1, delete "any of claims 1 to 10" and substitute therefor --Claim 1--.

Claim 12, line 1, delete "any of claims 1 to 11" and substitute therefor --Claim 1--.

Claim 13, line 1, delete "any of claims 1 to 12" and substitute therefor --Claim 1--.

Claim 14, line 1, delete "any of claims 1 to 13" and substitute therefor --Claim 1--.

Claim 15, line 1, delete "any of claims 1 to 13" and substitute therefor --Claim 1--.

Claim 16, line 1, delete "any of claims 1 to 15" and substitute therefor --Claim 1--.

Claim 17, line 20, delete "any of claims 1 to 17" and substitute therefor --Claim 1--.

U.S. SERIAL NO. To Be Assigned (U S. National Phase  
of International Application No. PCT/EP99/02102)  
FILED ON: Herewith  
EXAMINER. To Be Assigned  
GROUP ART UNIT. To Be Assigned

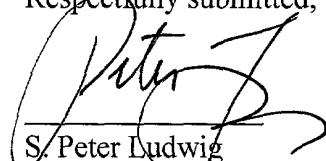
**REMARKS**

The specification has been amended to include proper headings in accordance with U.S. practice.

The claims have been amended to eliminate multiple claim dependencies.

Entry of this amendment is respectfully requested.

Respectfully submitted,



S. Peter Ludwig  
Registration No. 25,351  
Attorney for Applicants

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Method of Making Polymer Electrolyte Electrochemical Cells

5 This invention relates to a method of making polymer electrolyte electrochemical cells and to cells obtained thereby.

10 The recent development of electrochemical cells based on lithium containing negative electrode structures has allowed the fabrication of cells of high energy density. Cells have been obtained, which display energy densities beyond 200 Wh/l and even 250 Wh/l has been reported.

15 In order to reach such high energy densities, the capacity utilisation of the active materials in the cell should be high. As further high rate capabilities of the electrochemical cells are sought, electrolyte phases should provide low impedance.

20 Traditionally, high conductivity electrolytes have been liquid electrolytes and such electrolytes are used in lithium cells of intercalation compound electrodes. The positive electrode structures are based on transition metal oxides operating at a potential close to 4V vs. Li/Li<sup>+</sup>.  
25 Negative electrode structures of carbons and graphites may be applied, which reversibly intercalate lithium at a potential close to the potential of metallic lithium. Such cells are referred to as lithium-ion cells, as the active lithium is always in its ionic form. Alternatively,  
30 negative electrode structures of alloys such as Li-Al and Li-Sn may be used. Such cells will be referred to as lithium-alloy cells. All of the above configurations provide voltages close to 4V.

As high energy density and high rate capability imply reduced safety, an important objective in the development of such electrochemical cells has been to improve the safety aspects of the use of such cells.

The main improvement in terms of safety has been the substitution of carbon or alloy structures for the pure lithium metal negative electrode structures. During operation of lithium metal based negative electrodes, dendrites form, which penetrate the cell separator and shorten the cell. Although the risk of dendrite formation cannot be completely ignored in lithium-ion or lithium-alloy cells, especially during high-rate charging, the risk is strongly reduced compared to lithium metal cells.

Another problem associated with the liquid electrolytes traditionally applied is leakage of the electrolyte. The leakage may not only lead to cell failure but penetration of the corrosive fluid may destroy the electronic device in which the cell is used.

One approach to solve these problems has been the application of solid state electrolytes and the use of such electrolytes should eliminate the risk of dendrite formation and of electrolyte leakage.

US 5,296,318 to Bell Communication Research describes the use of a polymer electrolyte based on polyvinylidenefluoride-hexafluoropropylene copolymer, which is present in the electrolyte phase in an amount corresponding to 30-80% by weight of the electrolyte system. Electrochemical cells based on such polymer

electrolytes have significantly lower conductivity than cells based on a liquid electrolyte.

5 US 5,418,091 to Bell Communication Research describes a multistep process for the application of polymer electrolytes as described in US 5,296,318.

10 The above patents illustrate the problem of solid state electrolytes, and in particular of polymer electrolytes which are the best ambient temperature candidate since their conductivity is too low. Due to the low conductivity of the polymer electrolytes, the performance of the electrochemical cells in which they are applied is significantly reduced compared to liquid electrolyte cells.

15 US Patent No 5,688,293 to Oliver et al describes an electrochemical cell with a gel electrolyte which comprises a solvent and a gel forming polymer. The electrolyte was applied to the electrodes and gelled by heating.

20 US 5,705,084 to Joseph Kejha discloses a composite solid state or semi-solid state polymer electrolyte for batteries, capacitors and other electrochemical devices, wherein the electrolyte mixture contains polyethylene oxide, polyvinylidenefluoride/hexafluoropropylene, a salt and at least one aprotic liquid. In a preferred embodiment the electrolyte comprises polyvinylidenefluoride/hexafluoropropylene in an amount in the range 0.1-70% and polyethylene oxide in an amount in the range 0.5-70% by weight of the electrolyte system, respectively. The patent discloses the coating of electrodes with solutions of the above electrolyte, prepared at 60-90°C, and the subsequent thickening of the electrolyte upon solvent evaporation. The

patent, however, does not mention anything about changes in the rheological behaviour of the electrolyte other than those brought about by evaporation of the solvent.

5 WO 98/28812 to Danionics discloses a lithium secondary battery comprising an immobilized electrolyte containing one or more alkali metal salts, one or more non-aqueous solvents and an immobilizing polymer, wherein the immobilizing polymer is selected from the group consisting of cellulose acetates, cellulose acetate butyrates, cellulose acetate propionates, polyvinylidene fluoride-hexafluoropropylanes and polyvinylpyrrolidone-vinyl acetates with the proviso that in the case of polyvinylidene fluoride-hexafluoropropylanes, the polymer is present in an amount of at most 12% by weight based on the weight of the salts, solvents and polymer of the electrolyte system. The specification discloses a method for the preparation of a lithium secondary battery comprising the steps of solvent mixing, salt dissolution, addition of immobilizing polymer and sandwiching of the electrode between positive and negative electrodes. However, the specification does not mention the rheological behaviour of the electrolyte.

25 Therefore, there is a pressing need for polymer electrolytes and process technology therefor, which will provide electrochemical cells of high performance and safety, and which can be applied by a simple, low cost process.

30 It is thus an object of the present invention to provide such polymer electrolytes, which display performance similar to liquid electrolytes with improved safety, and

processes therefor, which are simpler than traditional processing of polymer electrolytes

5       The present invention relates to a polymer electrolyte which has a significantly lower polymer content than traditional polymer electrolytes but which can be processed according to a simple temperature scheme.

10     Surprisingly it has been found, that a range of polymer electrolytes exist, based for example on fluorocarbons, which upon heating to a certain dissolution temperature  $T_{dissol}$  produce low viscosity solutions. Such solutions are stable between room temperature and the above  $T_{dissol}$ . When additionally heated to a gelling temperature  $T_{gel}$ ,  $T_{gel} > T_{dissol}$ , they undergo a transition, such that upon cooling they form gels of significantly higher viscosity than the original solution.

15     Accordingly, the present invention provides a method for the preparation of a polymer electrolyte electrochemical cell using an electrolyte precursor, said precursor comprising one or more solvents, one or more salts and a polymer which dissolves in the solvent at a first temperature ( $T_{dissol}$ ) and which is capable of forming a gel on subsequent cooling following heating to a second temperature ( $T_{gel}$ ),  $T_{dissol}$  being lower than  $T_{gel}$ , which method comprises:

- 20
- (a) heating the electrolyte precursor to  $T_{dissol}$ ;
  - 25
  - (b) optionally cooling the electrolyte precursor;

- (c) incorporating the electrolyte precursor into the electrochemical cell;
- (d) heating the electrochemical cell to  $T_{gel}$
- 5 (e) cooling the polymer electrochemical cell to ambient temperature to bring about gelling of the polymer electrolyte.

10 As used herein, a gel is defined as a system of which the modulus of elasticity is higher than the modulus of loss, i.e. it has dominating elastic properties over viscous properties.

15 The processing scheme referred to above is preferably applied to polymer electrolytes with a polymer content in the range of 1-12% by weight of the electrolyte system. The electrolytes are then easily processable in that they are treated as liquid electrolytes until the final process step, during which the gelling takes place.

20 Thus, according to the present invention an electrolyte precursor comprising one or more solvents, one or more salts and a polymer having the features referred to above is heated to a temperature sufficient for the dissolution of the polymer in the solvent(s). This temperature,  $T_{dissol}$ , however, should not exceed the temperature, at which gelling of the polymer takes place upon subsequent cooling. Subsequently, the electrolyte precursor solution is incorporated into the electrochemical cell at a temperature in the range from room temperature to  $T_{dissol}$ . Following incorporation, the electrochemical cell is heated to a temperature  $T_{gel}$ . Upon subsequent cooling from  $T_{gel}$  to room

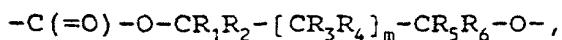
temperature, significant gelling of the electrolyte takes place, and the resulting polymer electrolyte has a significantly higher viscosity than the precursor.

5 In a preferred embodiment of the invention the polymer is a homopolymer or copolymer from the group of monomers of vinyl fluoride, vinylidenefluoride, trifluoroethylene, tetrafluoroethylene and hexafluoropropylene, preferably a copolymer of vinylidenefluoride and hexafluoropropylene, more preferably a copolymer of vinylidenefluoride and hexafluoropropylene of a molar weight in the range 50,000-10

10 500,000, more preferably 100,000-300,000, and a weight ratio of vinylidenefluoride and hexafluoropropylene in the range 80:20 to 90:10.

15 In a preferred embodiment of the present invention the electrolyte comprises one or more solvent(s) selected from the groups (a) to (e):

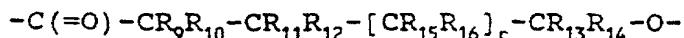
20 (a) alicyclic carbonates represented by the following general formula:



25 wherein each of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> independently represents hydrogen or a C<sub>1</sub>-C<sub>4</sub> alkyl group and m is 0 or 1, preferably ethylene carbonate or propylene carbonate;

30 (b) aliphatic carbonates represented by the general formula R<sub>7</sub>[OC(O)]<sub>p</sub>OR<sub>8</sub>, wherein each of R<sub>7</sub> and R<sub>8</sub> independently represents a C<sub>1</sub>-C<sub>4</sub> alkyl group, and p is an integer equal to 1 or 2, preferably dimethyl carbonate or diethyl carbonate;

(c) lactones in the form of cyclic esters represented by the general formula:



5 wherein each of  $\text{R}_9$ ,  $\text{R}_{10}$ ,  $\text{R}_{11}$ ,  $\text{R}_{12}$ ,  $\text{R}_{13}$ ,  $\text{R}_{14}$ ,  $\text{R}_{15}$  and  $\text{R}_{16}$  independently represents hydrogen or a  $\text{C}_{1-2}$  alkyl group and  $r$  is 0 or 1, preferably  $\gamma$ -valerolactone or  $\gamma$ -butyrolactone;

10 (d) esters represented by the formula  $\text{R}_{17}[\text{C}(\text{O})]\text{OR}_{18}[\text{OR}_{19}]_t$ , wherein each of  $\text{R}_{17}$ ,  $\text{R}_{18}$  and  $\text{R}_{19}$  independently represents hydrogen or a  $\text{C}_1\text{-C}_2$  alkyl group, and  $t$  is 0 or an integer equal to 1 or 2, preferably an acetate, more preferably (2-methoxyethyl)-acetate or ethyl acetate;

15 (e) glymes represented by the general formula  $\text{R}_{20}\text{O}(\text{R}_{21}\text{O})_n\text{R}_{22}$ , in which each of  $\text{R}_{20}$  and  $\text{R}_{22}$  independently represents a  $\text{C}_{1-2}$  alkyl group,  $\text{R}_{21}$  is  $-(\text{CR}_{23}\text{R}_{24}\text{CR}_{25}\text{R}_{26})-$  wherein each of  $\text{R}_{23}$ ,  $\text{R}_{24}$ ,  $\text{R}_{25}$  and  $\text{R}_{26}$  independently represents hydrogen or a  $\text{C}_1\text{-C}_4$  alkyl group, and  $n$  is an integer from 2 to 6, preferably 3,  $\text{R}_{20}$  and  $\text{R}_{22}$  preferably being methyl groups,  $\text{R}_{23}$ ,  $\text{R}_{24}$ ,  $\text{R}_{25}$  and  $\text{R}_{26}$  preferably being hydrogen or  $\text{C}_1\text{-C}_2$  alkyl groups, more preferably hydrogen.

25 In a preferred embodiment of the invention the salt of the electrolyte is selected from the group of alkali metal or ammonium salts of  $\text{ClO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{AsF}_6^-$ ,  $\text{PF}_6^-$  or  $\text{BF}_4^-$ , preferably  $\text{LiPF}_6$  and  $\text{LiBF}_4$ .

30 In a preferred embodiment of the invention the electrolyte precursor comprises solvent(s), salt(s) and polymer(s) in the compositional range from 63:25:12 to 94:5:1 percent of the total weight of the electrolyte system, preferably in the compositional range from 70:20:10 to 90:8:2 percent of

the total weight of the electrolyte system, more preferably in the compositional range from 75:17:8 to 88:8:4 percent of the total weight of the electrolyte system.

- 5 In a preferred embodiment of the invention the dissolution temperature is in the range 45-80°C preferably 60-80°C, more preferably 65-75°C, and the gelling temperature is in the range 75-100°C, preferably 80-90°C, with the proviso, that the gelling temperature should be higher than the  
10 dissolution temperature.

In a preferred embodiment of the invention the electrochemical cell comprises any one of the electrolytes as described above. The electrolyte may be confined in a separator consisting of a porous structure made of a polymer, preferably of polyethylene, polypropylene, polycarbonate or cellulose, the separator having a woven or non-woven structure having a pore size in the range of 10 x 10 nm to 1 x 1 mm and a thickness of 10-100 $\mu$ m, preferably 10-25 $\mu$ m. The cell further comprises a negative electrode structure comprising one or more compounds selected from the group of graphite, coke, mesocarbon microbeads, carbon black, aluminium, silicon or tin, and a positive electrode structure comprising one or more compounds selected from the group of lithium manganese oxides, lithium cobalt oxides and lithium nickel oxides.  
15  
20  
25

In a further preferred embodiment the electrodes display a porosity which is such as to allow diffusion of a relatively solvent-rich electrolyte phase into the pores of the electrodes, leaving a relatively polymer-rich electrolyte phase in the volume between the electrodes. Such separation of the electrolyte in a pore-phase and a  
30

bulk-phase further reduces the risk of electrolyte leakage. In the case of cell puncture, the low viscosity electrolyte phase will be bound in the pores and will not leak from the cell. Similarly, the high viscosity bulk phase will be bound between the electrodes.

In a preferred embodiment of the invention the incorporation of the electrolyte is applied on a wound cell, i.e. the winding of the cell is done prior to electrolyte impregnation. Such cell can be efficiently impregnated with the low viscosity electrolyte obtained from the first step of the present invention. The impregnation of wound cells further allows improved control of the solvent evaporation, i.e. the solvent composition is substantially unchanged during the process, even in the case of low boiling solvents such as dimethyl carbonate and diethyl carbonate.

In a further preferred embodiment of the invention the electrolyte incorporation is carried out by a simple pouring or injection process.

It has also been found that a further separation of the electrolyte can occur when the electrolyte is filled into cell-laminates and that this further separation can also be applied to advantageous effect. This separation arises because the gap between the electrode laminates is (or can be made) smaller than at least the largest polymer particles and the result is that electrolyte in the vicinity of the edge of the laminate and outside the laminate contains a larger amount of polymer than the electrolyte between the electrodes. This has the advantage that after gelling, the electrolyte in the vicinity of the

edge of the laminate is effectively solidified and thus prevents the possibility of short circuits in this sensitive area. It is thus possible to keep the electrolyte between the electrodes in a gelled state, or even in a liquid state, with minimum risk of leakage. The ratio of the distribution of polymer can be controlled by applying more or less pressure on the electrode laminate during the course of the filling process.

The invention also provides an electrochemical cell characterised by a negative electrode structure comprising one or more compounds selected from the group of graphite coke and mesocarbon microbeads and a positive electrode structure comprising one or more compounds selected from the group of lithium manganese oxides, lithium cobalt oxides and lithium nickel oxides, preferably lithium manganese oxide, and a gelled polymer electrolyte, 1-12% by weight, preferably 4-8% by weight, of the total weight of the electrolyte being said polymer, which is selected from the group of homopolymers and copolymers from the group of monomers of vinyl fluoride, vinylidenefluoride, trifluoroethylene, tetrafluoroethylene and hexafluoropropylene, preferably a copolymer of vinylidenefluoride and hexafluoropropylene, the electrochemical cell having been obtained by or being obtainable by a method as defined above.

### Examples

Example 1:

A lithium secondary battery was prepared from a negative electrode laminate of a polymer bound carbon coated onto a

copper current collector, a positive electrode laminate of a polymer bound lithium manganese oxide spinel coated onto an aluminium current collector, and an electrolyte.

5       The carbon was R-LIBA-A (product of Timcal, Switzerland).  
The lithium magnesium oxide spinel was prepared by a solid  
state reaction at 800°C from  $\text{Li}_2\text{CO}_3$  and  $\text{MnO}_2$  and had a  
specific capacity of 120 mAh/g. In the case of both  
10      electrodes, the polymeric binder was EPDM (ethylene  
propylene diene polymethylene).

15      The battery laminate was wound from the above negative and  
positive electrode laminates and a microporous polyethylene  
separator. The entire battery laminate was placed in  
plastic-coated aluminium "coffee-bag" container.

20      The electrolyte was prepared by mixing ethylene carbonate  
(EC) and diethyl carbonate (DEC) in a volume ratio of 2:1,  
adding  $\text{LiBF}_4$  and  $\text{LiPF}_6$  (60% to 40% by mole) to obtain a 1M  
solution of  $\text{LiBF}_4/\text{LiPF}_6$  in EC/DEC, heating the above liquid  
electrolyte solution to 70°C, and adding at this temperature  
5% by weight of polyvinylidene fluoride-hexafluoropropylene  
(PVDF/HFP) (KYNERFLEX 2822 from Elf Atochem) to the  
solution to obtain a 5% by weight solution of PVDF/HFP in  
25      1M  $\text{LiBF}_4/\text{LiPF}_6$  in EC/DEC. The polymer electrolyte was  
stirred at 70°C for 10 minutes before cooling to room  
temperature.

30      During these last stages, in the temperature range room  
temperature -70°C, the polymer electrolyte is in a liquid  
state.

The liquid polymer electrolyte was injected into the battery laminate at ambient temperature. Subsequently, the battery was heated to 85°C for ten minutes. The battery was allowed to cool to room temperature.

5

At this stage, the polymer electrolyte had gelled, displaying in the bulk phase between the electrodes a viscosity significantly higher than that observed for the original polymer electrolyte.

10

The battery prepared had an active electrode area of 365 cm<sup>2</sup> and, subsequent to charging to 4.2V, an internal impedance of 49 mΩ at 1kHz. When cycled between 4.2V and 2.5V at 500 mA, the battery displayed an initial capacity of 358 mAh. After 400 cycles, the capacity was 299 mAh, say 84% of the initial capacity. At 1.25A discharge rate, an initial capacity of 210 mAh was observed.

15

Upon nail penetration ( $\varnothing=5\text{mm}$ ,  $F=6000\text{N}$ ) the battery short-circuited, however, no leakage of electrolyte was observed on the surface of the battery upon visual inspection.

20

#### Comparative Example 1a:

25

A battery laminate was produced and packed according to example 1 and liquid state polymer electrolyte was prepared also according to example 1.

30

The liquid polymer electrolyte was injected into the battery laminate at room temperature. Compared to example 1, the battery was not heated subsequent to the electrolyte injection.

The battery having the same dimensional characteristics as the battery of example 1, had an internal impedance of 42 mΩ at 1kHz. When cycled between 4.2V and 2.5V at 500 mA, the battery displayed an initial capacity of 408 mAh.

5 After 400 cycles, the capacity was 343 mAh, say 84% of the initial capacity. At 1.25A discharge rate, an initial capacity of 280 mAh was observed.

10 Upon nail penetration ( $\varnothing=5\text{mm}$ ,  $F=6000\text{N}$ ) the battery short-circuited. Leakage of electrolyte was observed on the surface of the battery upon visual inspection.

Comparative example 1b:

15 A battery laminate was produced and packed according to example 1.

20 The electrolyte was prepared by mixing ethylene carbonate (EC) and diethyl carbonate (DEC) in a volume ratio of 2:1, adding LiBF<sub>4</sub> and LiPF<sub>6</sub> (60% to 40% by mole) to obtain a 1M solution of LiBF<sub>4</sub>/LiPF<sub>6</sub> in EC/DEC, and adding at room temperature 5% by weight of polyvinylidene fluoride-hexafluoropropylene (PVDF/HFP) (KYNERFLEX 2822 from Elf Atochem) to the solution to obtain a 5% by weight solution of PVDF/HFP in 1M LiBF<sub>4</sub>/LiPF<sub>6</sub> in EC/DEC. The polymer electrolyte was stirred at room temperature for 10 min.

25 during which partial dissolution of the polymer was observed.

30 The polymer electrolyte was injected into the battery laminate at ambient temperature. It was observed, that the distribution of electrolyte within the battery laminate was poorer compared to examples 1 and 1a, as undissolved

polymer was blocking the pores. Subsequently, the battery was heated to 85°C for ten minutes and the battery then allowed to cool to room temperature. The polymer electrolyte was gelled, displaying in the bulk phase between the electrodes a viscosity significantly higher than observed for the free polymer electrolyte.

The battery having the same dimensional characteristics as the batteries of examples 1 and 1a had an internal impedance of 150 mΩ at 1kHz. When cycled between 4.2V and 2.5V at 500 mA, the battery displayed an initial capacity of 280 mAh. After 100 cycles, the capacity was 176 mAh, say 63% of the initial capacity. At 1.25A discharge rate, an initial capacity of 138 mAh was observed.

Upon nail penetration ( $\varnothing=5\text{mm}$ ,  $F=6000\text{N}$ ) the battery short-circuited, however, no leakage of electrolyte was observed on the surface of the battery upon visual inspection.

Comparative example 1c:

A battery laminate was produced and packed according to example 1.

The electrolyte was prepared by mixing ethylene carbonate (EC) and diethyl carbonate (DEC) in a volume ratio of 2:1, adding  $\text{LiBF}_4$  and  $\text{LiPF}_6$  (60% to 40% by mole) to obtain a 1M solution of  $\text{LiBF}_4/\text{LiPF}_6$  in EC/DEC.

The electrolyte was injected into the above battery laminate at ambient temperature. No gelling of the electrolyte was observed.

The battery having the same dimensional characteristics as the battery of example 1, had an internal impedance of 38 mΩ at 1kHz. When cycled between 4.2V and 2.5V at 500 mA, the battery displayed an initial capacity of 421 mAh.

5 After 400 cycles, the capacity was 362 mAh, say 86% of the initial capacity. At 1.25A discharge rate, an initial capacity of 360 mAh was observed.

10 Upon nail penetration ( $\varnothing=5\text{mm}$ ,  $F=6000\text{N}$ ) the battery short-circuited. Leakage of electrolyte was observed on the surface of the battery upon visual inspection.

Example 2:

15 A lithium secondary battery was prepared as described in Example 1 except that the carbon was MCMB 10-28 (product of Osaka Gas Chemical Ltd.) and that the electrolyte was prepared by mixing ethylene carbonate (EC) and diethyl carbonate (DEC) in a volume ratio of 1:1 adding  $\text{LiBF}_4$  and  $\text{LiPF}_6$  (60% to 40% by mole) to obtain a 1M solution of  $\text{LiBF}_4/\text{LiPF}_6$  in EC/DEC, heating the above liquid electrolyte solution to 57°C, and adding at this temperature 2.5% by weight of polyvinylidene fluoride-hexafluoropropylene (PVDF/HFP) (KYNERFLEX 2822 from Elf Atochem) to the solution to obtain a 2.5% by weight solution of PVDF/HFP in 1M  $\text{LiBF}_4/\text{LiPF}_6$  in EC/DEC. The polymer electrolyte was stirred at 57°C for 10 minutes before cooling to room temperature.

20 25 30 During these last stages, in the temperature range room temperature to -57°C, the polymer electrolyte is in its liquid state.

The liquid polymer electrolyte was injected into the above battery laminate at ambient temperature. Subsequently, the battery was heated to 85°C for 10 minutes. The battery was allowed to cool to room temperature.

5

At this stage, the polymer electrolyte had gelled, displaying in the bulk phase between the electrodes a viscosity significantly higher than observed for the original polymer electrolyte.

10

The battery prepared had an active electrode area of 1500 cm<sup>2</sup> and, subsequent to charging to 4.2V, an internal impedance of 16 mΩ at 1kHz. When cycled between 4.2V and 3.0V at 3000 mA, the battery displayed an initial capacity of 2970 mAh. After 300 cycles, the capacity was 2550 mAh, say 86% of the initial capacity. At 6.0A discharge rate, an initial capacity of 2700 mAh was observed.

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Upon nail penetration ( $\phi=5\text{mm}$ ,  $F=6000\text{N}$ ) the battery short-circuited, however, no leakage of electrolyte was observed on the surface of the battery upon visual inspection.

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**Claims:**

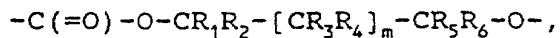
1. A method for the preparation of a polymer electrolyte electrochemical cell using an electrolyte precursor, said precursor comprising one or more solvents, one or more salts and a polymer which dissolves in the solvent at a first temperature ( $T_{dissol}$ ) and which is capable of forming a gel on subsequent cooling following heating to a second temperature ( $T_{gel}$ ),  $T_{dissol}$  being lower than  $T_{gel}$ , which method comprises:

- (a) heating the electrolyte precursor to  $T_{dissol}$ ;
- (b) optionally cooling the electrolyte precursor;
- (c) incorporating the electrolyte precursor into the electrochemical cell;
- (d) heating the electrochemical cell to  $T_{gel}$
- (e) cooling the polymer electrochemical cell to ambient temperature to bring about gelling of the polymer electrolyte

- 25 2. A method according to claim 1, in which said polymer is a homopolymer or copolymer from the group of monomers of vinyl fluoride, vinylidenefluoride, trifluoroethylene, tetrafluoroethylene and hexafluoropropylene.
- 30 3. A method according to claim 2, in which said polymer is a copolymer of vinylidenefluoride and hexafluoropropylene.

4. A method according to claim 3, in which said copolymer of vinylidenefluoride and hexafluoropropylene has a molecular weight in the range 50.000-500.000, more preferably 100.000-300.000, and a weight ratio of vinylidenefluoride and hexafluoropropylene in the range 80:20 to 90:10.
- 5
5. A method according to any of claims 1 to 4, in which the electrolyte comprises one or more solvent(s) selected from the groups (a) to (e):
- 10

(a) alicyclic carbonates represented by the following general formula:



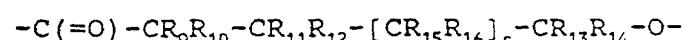
wherein each of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> independently represents hydrogen or a C<sub>1</sub>-C<sub>4</sub> alkyl group and m is 0 or 1, preferably ethylene carbonate or propylene carbonate;

20

(b) aliphatic carbonates represented by the general formula R<sub>7</sub>[OC(O)]<sub>p</sub>OR<sub>8</sub>, wherein each of R<sub>7</sub> and R<sub>8</sub> independently represents a C<sub>1</sub>-C<sub>4</sub> alkyl group, and p is an integer equal to 1 or 2, preferably dimethyl carbonate or diethyl carbonate;

25

(c) lactones in the form of cyclic esters represented by the general formula:



wherein each of R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub> and R<sub>16</sub> independently represents hydrogen or a C<sub>1-2</sub> alkyl group and r is 0 or 1, preferably  $\gamma$ -valerolactone and/or  $\gamma$ -butyrolactone;

5

(d) esters represented by the formula R<sub>17</sub>[C(O)]OR<sub>18</sub>[OR<sub>19</sub>]<sub>t</sub>, wherein each of R<sub>17</sub>, R<sub>18</sub> and R<sub>19</sub> independently represents hydrogen or a C<sub>1-C<sub>2</sub></sub> alkyl group, and t is 0 or an integer equal to 1 or 2, preferably an acetate, more preferably (2-methoxyethyl)-acetate or ethyl acetate;

10

(e) glymes represented by the general formula R<sub>20</sub>O(R<sub>21</sub>O)<sub>n</sub>R<sub>22</sub>, in which each of R<sub>20</sub> and R<sub>22</sub> independently represents a C<sub>1-2</sub> alkyl group, R<sub>21</sub> is -(CR<sub>23</sub>R<sub>24</sub>CR<sub>25</sub>R<sub>26</sub>)- wherein each of R<sub>23</sub>, R<sub>24</sub>, R<sub>25</sub> and R<sub>26</sub> independently represents hydrogen or a C<sub>1-C<sub>4</sub></sub> alkyl groups, and n is an integer from 2 to 6, preferably 3, R<sub>20</sub> and R<sub>22</sub> preferably being methyl groups, R<sub>23</sub>, R<sub>24</sub>, R<sub>25</sub> and R<sub>26</sub> preferably being hydrogen or C<sub>1-C<sub>2</sub></sub> alkyl groups, more preferably hydrogen.

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20

6. A method according to any of claims 1 to 5, in which the electrolyte comprises one or more salts selected

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from the group of alkali metal or ammonium salts of ClO<sub>4</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup> or BF<sub>4</sub><sup>-</sup>, preferably LiPF<sub>6</sub> and LiBF<sub>4</sub>.

30

7. A method according to any of the preceding claims, in which the electrolyte comprises solvent(s), salt(s) and polymer(s) in the compositional range from 63:25:12 to 94:5:1 percent of the total weight of the electrolyte system, preferably in the compositional

range from 70:20:10 to 90:8:2 percent of the total weight of the electrolyte system, more preferably in the compositional range from 75:17:8 to 88:8:4 percent of the total weight of the electrolyte system.

5

8. A method according to any of the preceding claims in which the electrolyte is confined in a separator consisting of a porous structure made of a polymer, preferably of polyethylene, polypropylene, polycarbonate or cellulose.
- 10 9. A method according to claim 8, in which the separator has a woven or non-woven structure having a pore size in the range of 10 x 10 nm to 1 x 1 mm.
- 15 10. A method according to claim 8 or 9, in which the separator has a thickness of 10-100 $\mu\text{m}$ , preferably 10-25 $\mu\text{m}$ .
- 20 11. A method according to any of claims 1 to 10, in which the electrochemical cell has a negative electrode structure comprising one or more compounds selected from the group of graphite, coke, mesocarbon microbeads, carbon black, aluminium, silicon or tin, preferably graphite, mesocarbon microbeads, coke or carbon black, more preferably graphite or mesocarbon microbeads, and a positive electrode structure comprising one or more compounds selected from the group of lithium manganese oxides, lithium cobalt oxides and lithium nickel oxides, preferably lithium manganese oxides, more preferably lithium manganese oxide  $\text{LiMn}_2\text{O}_4$  of spinel structure.
- 25
- 30

12. A method according to any of claims 1 to 11, in which the dissolution temperature  $T_{dissol}$  is in the range 45-80°C, preferably 60-80°C, more preferably 65-75°C, and the gelling temperature  $T_{gel}$  is in the range 75-100°C, preferably 80-90°C, with the proviso, that  $T_{gel}$  should be higher than  $T_{dissol}$ .
- 5
13. A method according to any of claims 1 to 12, in which the electrochemical cell is wound prior to electrolyte impregnation.
- 10
14. A method according to any of claims 1 to 13, in which the electrolyte incorporation is carried out by pouring or injection.
- 15
15. A method according to any of claims 1 to 13, in which the electrodes display such a porosity which is such as to allow diffusion of a relatively solvent-rich electrolyte phase into the pores of the electrodes, leaving a relatively polymer-rich electrolyte phase in the volume between the electrodes.
- 20
16. A method according to any of claims 1 to 15 wherein the gap between electrode laminates of the electrochemical cell is smaller than at least the largest polymer particles so that the electrolyte in the vicinity of the edge of the laminate and outside the laminate contains a larger amount of polymer than the electrolyte between the electrodes.
- 25
- 30
17. An electrochemical cell having a negative electrode structure comprising one or more compounds selected from the group of graphite,

coke and mesocarbon microbeads and a positive electrode structure comprising one or more compounds selected from the group of lithium manganese oxides, lithium cobalt oxides and lithium nickel oxides, preferably lithium manganese oxide, and a gelled polymer electrolyte, 1-12% by weight, preferably 4-8% by weight, of the total weight of the electrolyte being said polymer, which is selected from the group of homopolymers and copolymers from the group of monomers of vinyl fluoride, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene and hexafluoropropylene, preferably a copolymer of vinylidene fluoride and hexafluoropropylene, said electrochemical cell being obtained by or being obtainable by a method as claimed in any of claims 1 to 17.



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Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: METHOD OF MAKING POLYMER ELECTROLYTE ELECTROCHEMICAL CELLS

**(57) Abstract**

The invention relates to a method for the preparation of a polymer electrolyte electrochemical cell using an electrolyte precursor, said precursor comprising one or more solvents, one or more salts and a polymer which dissolves in the solvent at a first temperature ( $T_{dissol}$ ) and which is capable of forming a gel on subsequent cooling following heating to a second temperature ( $T_{gel}$ ),  $T_{dissol}$  being lower than  $T_{gel}$ , which method comprises: (a) heating the electrolyte precursor to  $T_{dissol}$ ; (b) optionally cooling the electrolyte precursor; (c) incorporating the electrolyte precursor into the electrochemical cell; (d) heating the electrochemical cell to  $T_{gel}$ ; (e) cooling the polymer electrochemical cell to ambient temperature to bring about gelling of the polymer electrolyte. Preferably the polymer is a homopolymer or copolymer from the group of monomers of vinyl fluoride, vinylidenefluoride, trifluoroethylene, tetrafluoroethylene and hexafluoropropylene.

**Combined Declaration for Patent Application and Power of Attorney (Continued)**  
 (Includes Reference to PCT International Applications)

 ATTY'S DOCKET NUMBER  
**2954/0H643**

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

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UNDER 35 U.S.C. 120:**

<b>U.S. APPLICATIONS</b>		<b>STATUS (Check one)</b>		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED

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PCT APPLICATION NO.	PCT FILING DATE	U.S. SERIAL NUMBER ASSIGNED (if any)

**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following attorney(s) and/or agents to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. Morris Relson #15,108, Gordon D. Coplein #19,165, William F. Dudine, Jr. #20,569, Michael J. Sweedler #19,937, S. Peter Ludwig #25,351, Paul Fields #20,298, Joseph B. Lerch #26,936, Melvin C. Garner #26,272, Ethan Horwitz #27,646, Beverly B. Goodwin #28,417, Adda C. Gogoris #29,714, Martin E. Goldstein #20,869, Bert J. Lewen 19,407, Henry Sternberg #22,408, Peter C. Schechter #31,662, Robert Schaffer #31,194, David R. Francescani #25,159, Robert C. Sullivan, Jr. #30,499, and Joseph R. Robinson #33,448, Anne E. Zitron #41,391.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patents issuing thereon.

SIGNATURE OF INVENTOR 201	SIGNATURE OF INVENTOR 202	SIGNATURE OF INVENTOR 203
<i>Martin Jor</i> DATE January 13, 2001	<i>S. Peter Ludwig</i> DATE January 12, 2001	<i>S. Peter Ludwig</i> DATE January 23, 2001

**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY**

(Includes Reference to PCT International Applications)

<b>ATTORNEY DOCKET NUMBER 2954/0H643</b>
--

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed for and which a patent is sought on the invention entitled:

**METHOD OF MAKING POLYMER ELECTROLYTE ELECTROCHEMICAL CELLS**

the specification of which (check only one item below):

- is attached hereto.  
 was filed as United States application

Serial No. \_\_\_\_\_

on \_\_\_\_\_

and was amended

on \_\_\_\_\_ (if applicable).

- was filed as PCT international application

Number PCT/EP99/02102

on March 29, 1999

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

**PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:**

COUNTRY (if PCT indicate PCT)	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 U.S.C. 119
GREAT BRITAIN	9806831.5	30 March 1998	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO